Neutral Layer Material Filtration for Directed Self Assembly Lithography

Toru Umeda*, Tasuku Matsumiya, Hitoshi Yamano, and Shuichi Tsuzuki

*SLS Global Technical Support, Nihon Pall Ltd., 46 Kasuminosato, Ami-machi, Inashiki-gun, Ibaraki 300-0315, Japan

bNext Generation Material Development Div., Research & Development Department, Tokyo Ohka Kogyo Co., Ltd., 1590, Tabata, Samukawa-machi, Koza-gun, Kanagawa 253-0114, Japan

Besides block copolymer, gel defects in neutral layer is another concern in directed self assembly lithography. To find appropriate filtration, we studied gel reduction in neutral layer materials. The test includes coating defectivity evaluation and gel removal test using various materials of filter membrane and neutral layer materials varied in monomer proportion of the polystyrene-random-poly(methyl methacrylate) (PS-PMMA) copolymer. Practical results using real world fluids and filters are obtained on the basis of collaboration. As a result, for intermediate PS content materials, Nylon 6,6 5 nm filter is found to be appropriate for gel reduction based on both coating defectivity and gel removal testing results. For relatively high PS content material, both Nylon 6,6 5 nm and HDPE 2 nm are recommended also based on the results. The mechanism of the gel removal is schemed based on hydrophilic interaction between Nylon 6,6 and hydrophilic part of the polymer.

Keywords: neutral layer, filtration, directed self assembly lithography, nylon 6,6

1. Introduction

Directed self assembly lithography (DSAL) is studied actively as a candidate for next generation lithography. Defectivity is one of the key concerns for DSAL and gel like contaminants in the material contribute largely to it as well as process-induced dislocations [1,2]. We have investigated PS-PMMA block copolymer (BCP) filtration in terms of its impact on the polymer characteristics and gel/metal reduction [3-6], because BCPs employed in DSAL are considerably different from conventional chemically amplified resists (CAR). We have found the filtration using Nylon 6,6 filter is the most effective among other membrane materials for reducing gels, which is probably derived from insufficient solubility of substantially large molecular weight of the BCPs. For metal reduction, Nylon 6,6 filter was also the most effective but greater reduction (>99.9% in Li, Mg and Al) was achieved with double step filtration combined with Nylon 6,6 and cation exchange filters.

Gel defects in neutral layer is another concern [1,2]. To find appropriate filtration on this material, Tokyo Ohka Kogyo (TOK) and Pall started a collaboration for studying gel reduction in neutral layer materials. The study contains coating defectivity evaluation and lab scale gel removal test using various filter membrane and various monomer proportioned neutral layer materials.

2. Experimental

2.1. Neutral layer materials

Hydroxyl-terminated polystyrene-random-poly(methyl methacrylate) (PS-PMMA) brush with three different PS content (Neutral layer material A, B and C, PS content low to high) in propylene glycol monomethyl ether
acetate (PGMEA) are provided by TOK. 1.5% solution is used for coating defect evaluation. For gel removal test, 10% polymer concentration is used because, in the preliminary study, the original 1.5% solution was found not to contain sufficient amount of gel to resolve the difference between the metrology parameters.

2.2. Test filters
Pall 5 nm rated asymmetric Nylon 6,6 filter, Pall 2 nm rated high density polyethylene (HDPE) filter and Pall 10 nm rated polytetrafluoroethylene (PTFE) filter are used. For coating defectivity, a point-of-use filter capsule with ~1300 cm² of filtration area is used. For gel removal testing, 47 mm diameter disk is used.

2.3. Track etch membrane
A hydrophilic polyimide track etch membrane (pore diameter = 30 nm, thickness = 12 μm and pore density = 6×10⁹ /cm²) purchased from it4ip is used to evaluate the gel amount in the test filter effluents. Prior to the testing, flow rate of the track etch membranes is measured by passing PGMEA to select membranes with consistent flow.

2.4. Coating defectivity
Test fluids filtered using test filters are coated on bare silicon wafers. Particle measurements are collected using a KLA-Tencor Surfscan SP2 inspection system.

2.5. Gel removal test
Test stand for the gel removal test is shown in Figure 1. Test fluid is passed through the test filters (2.2.) with applying 50 kPa of the inlet pressure to obtain effluents. An influent and the test filter effluents are then further filtered using track etch membrane (2.3.) with applying 200 kPa of the inlet pressure to determine cleanliness of the test filter effluents. The flow decay (=clogging) in the track etch membrane filtration indicates the cleanliness of the test filter effluent.

3. Results and Discussion
3.1. Coating defectivity
Figure 2 shows the results of neutral layer coating defectivity vs. filters. As a result, particle counts with using Nylon 6,6 5 nm and HDPE 2 nm filters are below the target value for all the neutral layer materials. Whereas with PTFE 10 nm filter, the target defectivity is not accomplished. The overall difference between Nylon 6,6 5 nm filter and HDPE 2 nm filter is not significant but in Neutral layer material A and B, Nylon 6,6 5 nm filter showed slightly lower counts than HDPE 2 nm filter. In Neutral layer material C, HDPE 2 nm filter is slightly better than Nylon 6,6 5 nm filter.

3.2. Gel removal test
Figure 3 shows the throughput vs. time in constant pressure filtration for influent and effluents of filtration test using track etch membrane. The results indicate the gel removal in the filtration test using test filters (Nylon 6,6 5 nm and HDPE 2 nm filters). As a result, flow decay of the track etch membrane on test filter effluents are lower than influential for all the tests. This indicates
that the factor for the clogging such as gel or particle are less in the test filter effluents than the influent. In Neutral layer material A and B, the effluent cleanliness of the Nylon 6,6 5 nm filter is better than HDPE 2 nm filter. In Neutral layer material C, HDPE 2 nm filter is slightly better than Nylon 6,6 5 nm filter but the difference is not significant.

3.3. Coating defectivity vs. gel removal test
In the results of coating defectivity on Neutral layer material A and B, Nylon 6,6 5 nm filter is slightly better than HDPE 2 nm filter. This trend is clearly supported by the gel removal tests and for this reason, can be interpreted as significant. In the results of coating defectivity on Neutral layer material C, HDPE 2 nm filter is slightly better than Nylon 6,6 5 nm filter, and this trend is also supported by the gel removal test.

3.4. Mechanism on adsorption
In the PS-r-PMMA, solubility of the hydrophobic PS part in PGMEA is lower than hydrophilic PMMA part. Gels potentially generated with aggregation of low solubility molecule should exist with the soluble part at the surface to mitigate the surface potential as schemed in Figure 4. If the PS content is lower, sufficient amount of the PMMA in the gel cover the surface and this drives the adsorption on Nylon 6,6 filter by hydrophilic interaction, as observed in Neutral layer material A and B for both coating defectivity and gel removal test. In contrast, if PS content is relatively higher, PS more appears at the surface and this prevents the hydrophilic interaction and the gel removal performance in HDPE will become relatively higher, as observed in Neutral layer material C.

4. Conclusion
Results in this study is practical because the tests are conducted with the real fluids and the filters, and is accomplished on the basis of TOK-Pall collaboration.
In particular, for Neutral layer material A and B, Nylon 6,6 5 nm filter is found to be appropriate for gel reduction based on both coating defectivity and gel removal testing results. And for Neutral layer material C,
both Nylon 6,6 5 nm and HDPE 2 nm filters are recommended also based on the results. The mechanism of the gel removal is schemed based on hydrophilic interaction between Nylon 6,6 and hydrophilic part of the polymer.

References

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